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Towards coupling dispersive liquid-liquid microextraction with hollow fibre liquid phase microextraction for extraction of organic pollutants of agricultural origin

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ABSTRACT

Liquid-based miniaturized techniques have received a lot of attention recently resulting in the development of the liquid phase microextraction (LPME) and dispersive liquid-liquid microextraction (DLLME) techniques each offering unique benefits over the other technique. Herein we report a combination of the two techniques for the extraction of hexestrol and atrazine from aqueous systems. The method sets off with the DLLME thereafter a hollow fibre filled with the organic solvent is introduced for the extraction of the pre-extracted analytes in the dispersed organic solvent. The method was modified further by introducing a second extracting solvent in place of the disperser solvent. Under the optimum conditions, namely, toluene in the acceptor phase, 1:1 chloroform:toluene (v/v) as a dispersed solvent, 15% NaCl, with the 15 min extraction time, the method achieved satisfactory enrichment factors (87- and 62-fold); sufficiently low detection limits of 0.018 μg/mL and 0.016 μg/mL using the flame ionization detector, while 0.072 and 0.063 ng/mL were obtained using single ion monitoring mass spectrometry detector, for atrazine and hexestrol, respectively; with sufficient linearity ($R^2 \geq 0.9959$). Although the compounds were not detected in the river water sample, satisfactory recoveries (111–115%) were achieved indicating the method did not suffer any negative matrix effect.

1. Introduction

As the search for ways of improving the quality of life in general, new chemicals enter the fore. The most common among these chemicals are agro-chemicals, such as pesticides and fertilizers that are used to improve agricultural production. However, these chemicals end up in places that they were not intended to be where they pose a challenge to environmentalists, public health practitioners and analytical chemists [1,2]. Since some of these chemicals have a potential to bio-accumulate [3], it is important for environmentalists to keep up with the pace at which these chemicals are being produced, so that they can be detected even in the ultra-trace level concentrations to help mitigate their build-up in the eco-system. Sadly, the adoption of the newly developed techniques into the official methods is reportedly very slow, thus worsening the state of pollution from these chemicals [4].

The role of analytical chemists in this conundrum is to develop new efficient, robust and affordable methods that can be applied for the analysis of these important chemicals. Of the two main aspects, namely, instrumental development and sample preparation, the latter is the most feasible to the poorly resourced economies where technological advancement is not at its best. Sample preparation techniques have a capacity to improve the detectability of the otherwise, non-detectable compounds through either converting them to analysable derivatives or pre-concentration to the detectable levels. To this effect, there are mainly two classes based on the physical states of the materials used, namely, solid-based and liquid-based techniques.

In an effort to replace the copious amounts of the hazardous organic solvents used in liquid-based techniques, a solid-based technique commonly known as solidphase extraction was developed which later gave rise to its miniaturised form - solidphase micro-extraction [5]. Similar strides have been made in the liquid-based techniques leading to the establishment of the three main classes of miniaturised liquid-based techniques: drop-based techniques [6], membrane-supported [7] techniques and lately the dispersed solvent-assisted techniques [8]. Each of these techniques

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has been a focus of studies resulting in the birth and evolution of different formats. The drop-based techniques have arguably seen more evolution resulting in the following different formats: drop-to-drop variants [9], freely suspended droplet [10], film-based extraction [11] and the bubble-assisted variants [12,13]. Despite this evolution, the drop-based techniques have not yet been officially accepted for broad application for routine analysis arguably due to its manual intensity requiring good hand-eye coordination to carefully pipette immiscible layers of similar appearance [14].

Liquid-phase microextraction (LPME) is a good candidate for the application in complex matrices like environmental samples given that the membrane already acts as a selective sampler by providing some degree of size exclusion depending on the pore size irrespective of the affinity of the acceptor/extracting phase for the analytes, thereof. On the other hand, dispersive liquid-liquid microextraction (DLLME) offers the unbeatably quick extraction rates although sadly this is accompanied by extensive human manipulation leading to extra steps that could be a gateway for inadvertent contamination, sample loss and poor automation. Interestingly, there are no reports where any of these somewhat seemingly complementary variants have been combined safe for an approach where a somewhat modified dispersive liquid-liquid microextraction was coupled to headspace SPME extraction, using the pre-dispersed solvent to drive the analytes into the headspace for eventual sampling with the SPME fibre [15], and another one where the pre-dispersed solvent was separated into a different vial and evaporated completely and sampled with the SPME for eventual analysis [16]. Herein we report the attempt to couple LPME with the DLLME where the hollow fibre is directly immersed in to the aqueous solution containing hexestrol and atrazine as model analytes whose introduction into the environment is linked to agricultural practices. The modification takes advantage of the fast extraction kinetics of the DLLME while eliminating the extra steps required in DLLME such as precipitating the solvent after the extraction.

2. Experimental

2.1. Chemical and standard solutions

Atrazine (1-Chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine, CAS 1912-24-9) was purchased from (Chem Service, Pennsylvania, USA), hexestrol (4,4′-(1,2-diethylethylene) diphenol, CAS 84-16-2) was obtained from Dr Ehrenstorfer GmbH (Augsburg, Germany), diphenylamine was obtained from Sigma Aldrich (Johannesburg, South Africa) while all the HPLC grade solvents: methanol, toluene, chloroform were obtained from Riedel-de Haën (Seelze, Germany). NaCl was obtained from ACE (Johannesburg, South Africa). The distilled water was prepared in-house. The Accruel Q3/2 PP polypropylene hollow fibre membrane with the dimensions of 600 μm (internal diameter) × 200 μm (wall thickness) × 0.2 μm pore size was obtained from Membrana GmbH (Wuppertal, Germany) and cut in 1-cm strips using a measuring ruler and a pair of scissors.

The standard solution of the concentration 10 mg/mL was prepared by dissolving the pre-weighed amounts of the standards in 1-mL ethanol. This solution was diluted serially to achieve lower concentrations as necessary using the same ethanol or water. All the solutions were stored in the refrigerator at temperature below 5 °C when not in use.

2.2. Instrumentation

Most of the development work was carried out using a Varian 3800 Gas Chromatograph (California, USA) equipped with a flame ionization detector and a 30 m × 1 μm × 0.53 mm SGE-BP5 (5% phenyl-95%dimethyl-polysiloxane) capillary column (Texas, USA). Nitrogen gas (5.0 Grade) was used as a carrier gas and maintained at 5 mL/min while hydrogen and air were used for the detector. The injector and detector temperature were set at 250 °C and 200 °C respectively. The column was held at 100 °C for 2 min, then ramped at 20 °C/min to 300 °C and held for 3 min to achieve a total run time of 15 min.

For the low level concentrations and validation experiments, a Shimadzu QP2010 GC-MS (Kyoto, Japan) fitted with an Rtx-5ms capillary column of 30 m × 0.25 mm × 0.25 μm dimensions was used with the same gas chromatograph settings as above. The mass spectrometer settings included the electron impact voltage of 70 eV with acquisition carried out relative to the tune file, the ion source temperature set 200 °C and the interface set 240 °C. Initially the acquisition was set on full scan with the *m/z* values in the range 50–350 for identification, followed by selected ion monitoring using the *m/z* values 135 (207,107) for hexestrol and 200 (205) for atrazine, the values in the parentheses representing the qualifying ions.

2.3. Water samples

Two water samples were collected in 50-ml Schott bottles from Liphiring River running about 3–4 km North West of the Roma campus few meters upstream of the road bridge to avoid potential pollution from the traffic. These samples were stored in a refrigerator at 5 °C. There was no sample preparation steps undertaken to the water samples except employing the optimized conditions are set out in the prior sections: addition the ideal amount of NaCl, chloroform and toluene to obtain optimum extraction conditions. Thereafter these samples were spiked with the analytes and the recovery was determined thereof.

2.4. Extraction procedure

For the extraction, firstly the aqueous sample of the mixture of the analytes was spiked with an organic solvent (toluene) and shaken vigorously to achieve homogeneity. Thereafter it was allowed to stand as the 1 cm long hollow fibre membrane filled with the extracting solvent (pre-spiked with the diphenylamine internal standard) fitted at the tip of the Hamilton® syringe was introduced carefully into the solution. After the extraction time had elapsed, 3 μL was withdrawn and injected into the gas chromatograph for analysis. Different parameters, namely, effect of the dispersed organic solvent, effect of changing disperser solvent with the second extracting solvent, effect of ionic strength, extraction time were assessed for their effect on the extraction in a univariate fashion.

The optimized method was further assessed for repeatability (both inter- and intra-vial), linearity, limits of detection as well as its applicability to field samples using a river water sample. All the analyses were carried out in triplicate unless otherwise stated under the relevant section of the results and discussions.

3. Results and discussions

3.1. Optimization of extraction conditions

3.1.1. Determination of the effective organic solvent volume

From the chemical structures of the compounds toluene was deemed the most suitable of the available solvents owing to the aromatic ring in the analytes, together with its water immiscibility. The task was then to determine the optimum volume of toluene that would effectively extract and preconcentrate the analytes.

Several 1-mL aqueous working solutions spiked at 5 μg/mL for the analytes were spiked with different volumes of toluene to determine the optimum volume, the results of which are presented in Fig. 1 for the 10-min extractions. Since the internal standard was used the responses represent the ratios of the peak areas for the respective analytes.

As can be seen from Fig. 1, the extraction efficiency increased with increasing volume of toluene and reached a maximum at 50 μL then dropped when increasing up to 100 μL. This shows that high volumes greater than 50 μL lead to the dilution of extracted analytes as the volume is high and a limited amount of the analytes migrate into the fibre. The volume of 50 μL was therefore considered optimum and was used for further extractions.

3.1.2. Effect of adding a dispersing solvent to the aqueous solution

Recently DLLME has been developed as an improvement on the extraction rate/speed as it increases the dispersion of the organic solvent through the aqueous solution. Different volumes of ethanol (dispersing solvent) were used and spiked into the aqueous solution together with toluene (as extracting solvent). Fig. 2 shows the effect of adding ethanol to the aqueous solution on the extraction of the analytes.

It can be seen from Fig. 2 that the addition of ethanol did not show any significant improvement to the extraction efficiency. This may be attributable to the high solubility of ethanol in water and as a result it renders the analytes more soluble in the aqueous solution; thus reducing their extractability into the fibre.

3.1.3. Effect of addition chloroform in place of the dispersing solvent

Having observed a decrease in efficiency while using methanol-

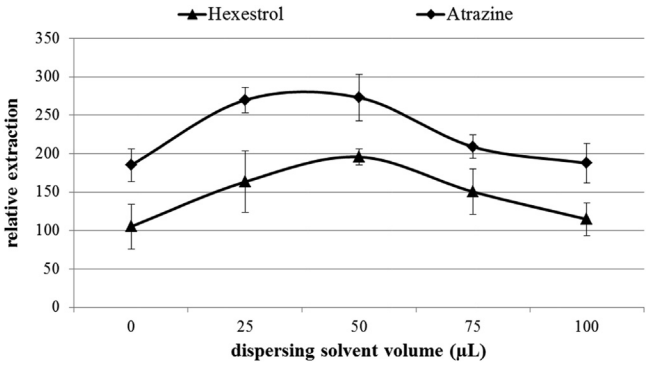

Fig. 1. The effect of varying the pre-dispersed solvent volume on extraction of the analytes.

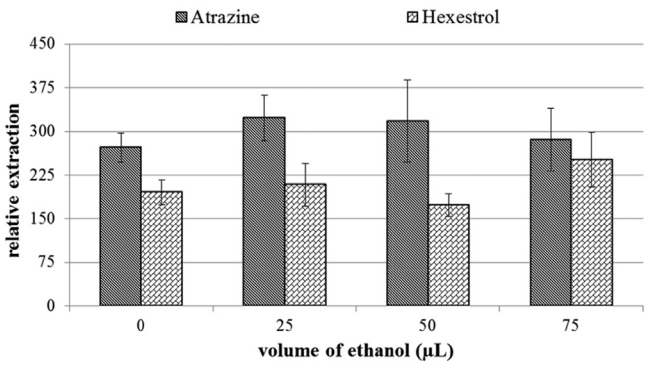

Fig. 2. The effect of increasing volume of the ethanol (the dispersing solvent) on extraction of the analytes.

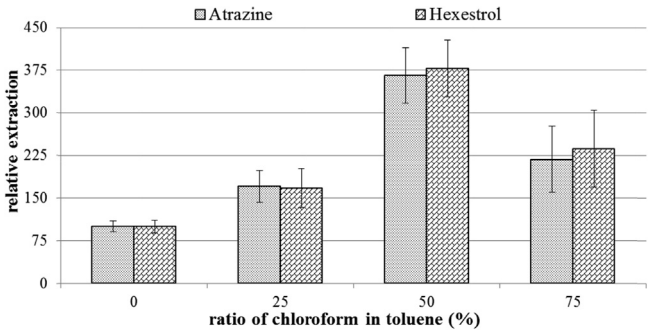

Fig. 3. The effect of adding chloroform in the toluene on the extraction (referenced against 100% toluene).

spiked toluene, it was prudent to consider a different solvent-perhaps a less soluble solvent in water could perform better. A mixture of chloroform and toluene has been reported to increase the extraction efficiency of hexestrol although it was reported in a drop-based method [17,18]. Therefore, it was considered prudent to investigate the effect of mixing the dispersed solvents and to determine the optimum mixing ratio of the two solvents. Fig. 3 shows the effect of addition of different ratios of chloroform to the toluene prior to spiking into the aqueous solution.

From Fig. 3, it can be seen that the extraction increased with the increasing ratio of chloroform up to a ratio of 1:1, thereafter decreased. This could be attributed to the polarity of chloroform compared to toluene, affording more solubility for the analytes. However as the volume of chloroform was increased, some organic solvent sedimentation was observed. Interestingly, little or no loss in extraction efficiency was observed as can be seen in Fig. 3, except for the loss of precision as evidenced by the larger error bars, although not very clear due to the referencing against pure toluene. As the volume of chloroform increased, there was an increase in the amount of sediment, hence some analytes were lost with the sediment, hence a drop in precision, although the extraction efficiency somewhat stayed almost unaffected. The other observation was that with the increased volume of chloroform, the membrane became heavier and it became more difficult to suck the extracting solvent back into the syringe as the membrane sometimes detached and fell into the solution indicating that the chloroform that was pre-dispersed into the aqueous solution was also being extracted with the analytes.

Following this, it was subsequently determined that the maximum volume of the 1:1 chloroform:toluene mixture that does not lead to immediate sedimentation was about 25 μL (results not shown here) hence this volume was used as an ideal volume replacing the 50 μL determined earlier while preserving the 1:1 ratio for the mixture for the subsequent experiments.

3.1.4. Effect of ionic strength of the aqueous solution on extraction efficiency

The addition of salt is traditionally used to increase the extraction efficiency due to the salting out effect. This effect has been accounted to decreasing the solubility of analytes in the aqueous phase and enhancing partitioning into the organic phase. This effect was studied by obtaining 1 mL of the working solution and adding the above determined mixing ratio of chloroform - toluene then adding varying the amount of NaCl in the range of 0–20% (m/v). The effect of varying NaCl in the aqueous solutions is shown in Fig. 4 with the results drawn relative to the extraction of the solution without any NaCl (0% NaCl).

As can be seen, the pre-concentration increased with increasing

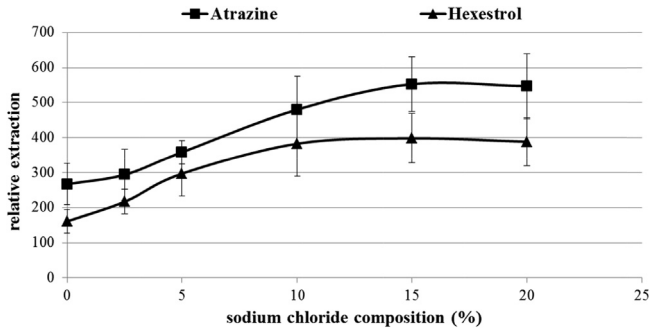

Fig. 4. The effect of addition of sodium chloride salt addition on extraction of the analytes.

addition of NaCl and peaked at 15%. The increase in extraction is attributed to the commonly established salting out phenomenon. The loss is extraction at higher concentrations of NaCl could be attributed to the salting out of the organic solvent out of the aqueous solution as reported elsewhere in literature that as the amount of NaCl was increased, some organic solvent was observed floating above the solution consequently negating the salting-out effect benefit, hence a reduction in extraction efficiency [19]. This separation of the organic solvent would therefore result in the transfer of analytes out of the aqueous solution with the separated organic solvent leading to a reduction in their extractability. Therefore the 15% NaCl was chosen to be the composition providing an optimum ionic strength yielding the highest extraction pre-concentration.

3.1.5. Exploration of the extraction time using the optimised conditions

Owing to the fact that the LPME system exposes a much lower surface area to volume ratio, it shows less mass transfer compared to the dispersive LLME, which usually achieves maximum extraction within seconds due to vigorous mixing. Without stirring, LPME usually shows much slower extraction kinetics peaking typically in the time periods in the range 40–60 min depending on the type of the analytes in the solution being extracted [20,21]. Fig. 5 shows the extraction-time profile for the two analytes under the optimised conditions.

It is evident that the extraction for both analytes peaked at around 15 min after which it remains almost constant. This time is significant given the simple LPME peaks after about four times this time – about 60 min [20]. This therefore is an improvement in the extraction kinetics. The extraction of 15 min was therefore chosen as an ideal extraction time without stirring – which could possibly decrease this time even further.

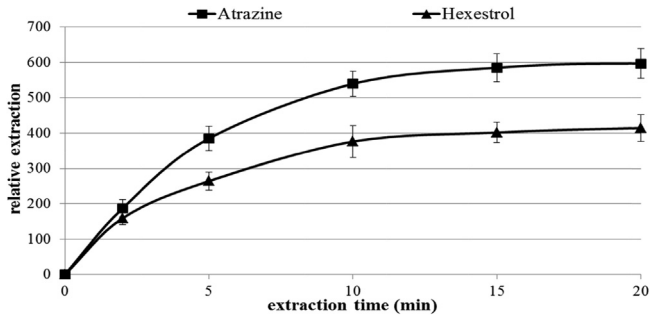

Fig. 5. The extraction-time profile for the two analytes under the optimised extraction conditions.

3.2. Method validation and quantitative analysis

The optimum conditions can be summarized as follows: spiking of sample solutions with 25 μL of a 1:1 toluene:chloroform, 15% (m/v) NaCl with the extraction time of 10 min. Under these conditions, the concentrations in the organic extracts were found to be higher than the original aqueous solutions by about 87 and 62 times for atrazine and hexestrol respectively. This therefore means that the enrichment factors – ratio of the concentration in the organic to that in the original aqueous solutions, of about 8700% and 6200% respectively were realised. These values are comparable to those reported for both DLLME and LPME techniques for atrazine [22], and also matches those reported for hexestrol, albeit in the drop-based methods [17,18,23].

Prior to quantitative analysis, it is worth determining the linearity of the method in order to enable correlation between the responses to the concentration of the analytes detected thereof. To assess this, different solutions (0.1–20 μg/mL) were prepared and extracted and their extraction responses were analysed using Microsoft® Excel Regression Analysis to determine linearity (coefficients of determination), regression equations (calibration equations) from which quantitative analysis can be carried out as well as estimating the limits of detection that can be achieved by this method. The repeatability of the method was assessed both for inter- and intra-vial by extraction of three different solutions (inter-vial repeatability) and extracting the same solution three times (intra-vial repeatability). The summary of all the determined parameters is presented in Table 1 including the recovery of these analytes after being spiked into the river water and extracted accordingly.

The method yielded sufficient linearity with the determination coefficients, $R^2 \geq 0.9959$, accompanied by the significantly low limits of detection for an FID detector, 0.018 μg/mL (atrazine) and 0.016 μg/mL (hexestrol); and these improved about three orders of magnitude to 0.072 ng/mL (atrazine) and 0.063 ng/mL (hexestrol) when employing the selected ion monitoring electron impact mass spectrometry (SIM EI-MS). These values are comparable to those reported elsewhere in literature [12,18,19]. The results further demonstrated that the method showed poor intra-vial repeatability (%RSD > 20%). A similar observation, poor to no intra-vial reproducibility, was made and reported elsewhere; albeit in a different approach while still the pre-dispersed solvents [15]. This was attributed to possible depletion of the pre-dispersed solvent in the earlier extractions changing the extraction dynamics and the equilibrium thereof for the subsequent extractions. A better repeatability (%RSD ≤ 11%) was achieved with the inter-vial assessment. However, these values can still be improved further with a more optimisation such as using the dynamic extraction that affords better mass transfer as well as using a less dense solvent than chloroform that seemed to have a somewhat negative effect in

Table 1
Some analytical data for the two analytes obtained under the optimised method.

Analytical data	Atrazine	Hexestrol
Regression equation	y = 95x + 7	y = 73x + 33
Linearity, R^2	0.9969	0.9959
Estimated LOD[a] (μg/mL)	0.018	0.016
Intra-vial repeatability (%)	20.7	23.0
Inter-vial repeatability (%)	10.7	11.0
Enrichment factor[b] (%)	8700	6200
Recover from river water[c] (%)	115 (9.7)	111 (10.8)

[a] LOD calculated from the equation, $\text{LOD} = \frac{3 \times \text{std error of intercept}}{\text{slope}}$.
[b] Enrichment Factor calculated from, $\%EF = \frac{C_{org}}{C_{aq}} \times 100\%$.
[c] The values in parentheses denote precision (% RSD) for triplicate analyses (n = 3).

terms of the extraction operation not necessarily the extraction efficiency itself.

Due to the unavailability of the certified reference materials, the accuracy validation was not carried out.

3.3. Analysis of real samples

Usually newly reported methods are tested for applicability in different real samples since most development is carried out using solutions prepared using pure solvent. To achieve this, 3 different water samples were used as controls, while the other three were spiked at the same level as the solutions prepared using distilled water and all these solutions were extracted under the optimised conditions and the samples were analysed both with the GC-FID and GC-MS. However both techniques could not detect any analytes. Importantly, those samples that were spiked with the standards showed equal or better extraction efficiencies, with recoveries of 102 and 115% respectively, without showing any negative matrix effect as expressed in Table 1. The statistical comparison of these two relative recoveries with those from the distilled water surrogates showed that these recoveries are equal within 95% confidence, indicating the higher values than 100% were consequence of normal experimental error, not attributable to the presence of the analytes in the river water sample.

4. Conclusions

This report demonstrated the potential of coupling the two liquid-based techniques offering the better of the two approaches. Most importantly, this is achieved without compromising the performance of each technique. This approach significantly reduced the extraction time required in the classical LPME from (30 min to an hour) to just 15 min with significant linearity ($R^2 \geq 0.9959$), sufficiently low limits of detection 0.018 and 0.016 μg/mL for flame ionisation detection and 0.072 and 0.063 ng/mL for mass spectrometric detection, the inter-vial repeatability (% RSD $\leq$ 11%). Interestingly, the method demonstrated the enrichment factors of 87-fold for atrazine and 62-fold for hexestrol relative to the surrogates prepared using distilled water, a remarkable feat for the LPME approach within such reduced extraction time. Despite not detecting any analytes in the river water sample that was used for real sample application, satisfactory recoveries (102 and 115% respectively) were still recorded demonstrating considerable tolerance to the matrix effect afforded by the river water matrix.

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